

SCIENCE FOR GLASS PRODUCTION

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FACTORS OF SURFACE AND VOLUMETRIC REACTIONS IN GLASS TECHNOLOGY PROCESSES

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Various phenomena and processes in glass production are considered taking into account surface and volumetric factors. Kinetic analysis of reactions of $K_2O - PbO - SiO_2$ system glasses with a reducing flame and the molding process under isothermal and non-isothermal conditions is carried out. The data obtained can be used for analysis and calculations of technological processes.

Technologies can evolve and be effectively improved only by understanding the physicochemical basis of technological processes. In this context, the present article offers examples of the physicochemical approach to analysis of complex phenomena and processes in glass production, taking into account the surface and the volumetric component. The expediency of this approach is determined by the fact that any heterogeneous process starts on the surface and then extends to the volumetric stage. This is true of both chemical processes and those in which physical factors prevail.

Experimental results can be interpreted using the probabilistic concept of formation of new phases, heterogeneities, etc., the theoretical principles of which are stated in [1–3].

Kinetic analysis is based on splitting a process into surface and volumetric stages, involving the determination of the rate constants and activation energies for each stage and relating them to the structural specifics of the reactants and the process conditions. Such analysis was applied in [4–6].

In the present paper, the kinetic analysis of glass technology processes is illustrated by the examples of heterogeneous chemical reactions in lead-silicate glasses and solidification of the glass melt in molding.

Studies of chemical reactions in glasses of the $K_2O - PbO - SiO_2$ system. Reducing chemical processes in lead-silicate glasses take place in flame treatment of glass during production of electric-vacuum devices and household glass, in the course of reactions between gases and the glass melt in melting, soldering parts to glass, two-stage fire polishing (USSR Inv. Certif. No. 429034), etc. Reducing chemical processes in glass were studied on the basis of the following glass composition (wt.%): 60 SiO_2 , 24 PbO , 16 K_2O .

A stabilized reducing flame was generated by natural-gas combustion. The temperature was measured by surface thermocouples.

The integral light absorption of samples in the visible spectrum range, which was registered by a spectrophotometer, was used to characterize the reduction process parameter. The surface conductivity was measured as well. In doing so, the kinetic principle of stopping the process at a certain moment was applied, and therefore, light absorption and electrical conductivity were measured at room temperature. Due to the rapid increment of viscosity in the surface layer of the glass sample under cooling, a state that is achieved at a certain moment of thermal treatment is reliably registered.

The kinetic analysis of the process was performed on the basis of the obtained experimental data.

Figure 1 represents kinetic curves for the light absorption of samples treated under reducing conditions at a tempera-

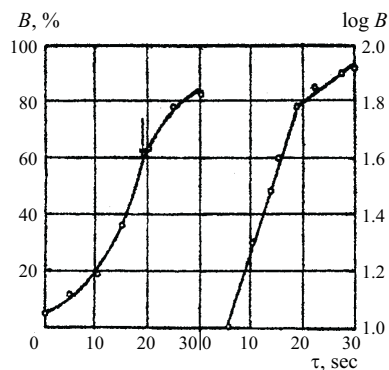


Fig. 1. Kinetic curve for light absorption B in glass treated in a reducing flame at a temperature of 815°C and its semilogarithmic anamorphosis.

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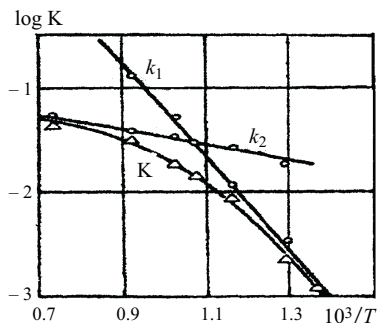


Fig. 2. Temperature dependence of the reduction process rate constants.

ture of 815°C in the surface layers. The arrow indicates the curve knee point. This point correlates with the maximum surface conductivity. The specific conductivity grows from 1.6×10^{-15} to 2.04×10^{-9} S/m.

The existence of the knee point is evidence of a two-stage process. In the first stage, as a consequence of surface chemical reactions, reduction of lead occurs in the atomic-dispersed form [7, 8]. The lead atoms in this case act as centers facilitating exchange of electrons. The glass surface acquires semiconducting properties with a substantial electron conduction component, which is indicated by the maximum conductivity. In the second stage, atomic lead aggregates in microparticles with glass interlayers between them, and the surface conductivity decreases due to the loss of the electron component. At the same time, reducing gases penetrate into the glass bulk and reduce the lead contained in the bottom layers. However, the semiconducting state with electron conduction is accomplished only for the surface layer, whereas the growth of light absorption is perceptibly retarded, which is indicated by the kinetic-curve shape after the knee point. In this stage of reduction, the increasing thickness of the reduced layer is accompanied by partial evaporation of lead from the surface layers. The retarded growth of light absorption is also related to the diffusion difficulties for the reducing gases as they penetrate into the glass.

The experimental data point to the diffusion-kinetic type of reduction process, and one can say that in the first stage, the process occurs in the kinetic region. Splitting of the kinetic curve into two segments and construction of semilogarithmic anamorphoses indicate that both reduction stages proceed according to the first order. The reduction rate constants for the two stages are 0.138 and 0.027 sec^{-1} , respectively.

The integral rate constant K for the diffusion-kinetic regime is found in the following way [9]:

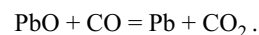
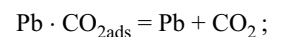
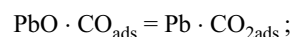
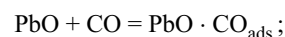
$$K = \frac{k_1 k_2}{k_1 + k_2},$$

where k_1 and k_2 are the constants of the chemical reaction and the diffusion process, respectively.

Determination of the kinetic characteristics of the process at various temperatures makes it possible to identify the temperature dependence of the rate of the process as a whole and in the boundary regions. This dependence for the process rate constant at different temperatures is shown in Fig. 2, where the temperature regions of the kinetic and diffusion processes are visible. The intersection point of the straight lines correlates with the temperature at which the rate constants of these two regimes are equal. With increasing temperature, the process is shifted toward the diffusion region, and with decreasing temperature, it is shifted toward the kinetic region.

The reduction process mechanism can be interpreted in the context of adsorption. As this process takes place on the glass surface, at first the reducing gas is adsorbed by the reacting surface, then oxygen breaks away from the lead complex and transits to the adsorbed reducing gas molecules, which is accompanied by the emergence of the reduced metallic lead phase, and finally, desorption of the formed gaseous product occurs.

The process of lead reduction on the surface can be represented in general form as follows:



A similar process takes place under the effect of hydrogen.

The specific structural function of lead in glass related to the high polarization capacity of the lead electron shell results in the formation of certain structurally defined lead-oxygen groups with relatively low force parameters. The bond energy in these groups is 75–163 kJ/mole, whereas this parameters in H_2 and CO amounts to 431 and 1071 kJ/mole.

The activation energy of the reducing reaction determined on the basis of kinetic data ($E_a = 86$ kJ/mole) is comparable to the energy of the $\text{Pb}-\text{O}$ bond, which is evidence of the decisive effect of the break rate of these bonds on the chemical reduction rate. When the reduction process is completed, metallic lead nuclei aggregate on the surface, and the distances between the enlarged particles increase. Electron exchange under such conditions becomes impossible, and the conductivity decreases due to the loss of the electron component.

Molding of glass articles. Measurements and calculations of viscosity and surface and interfacial tension at different temperatures were used to study the process of molding in various glass articles (float glass, small spheroid articles, bottles). The interfacial tension in the float process was determined using x-ray photography of a metallic drop under the glass layer.

The studies were carried out under both laboratory and industrial conditions, using industrial glass compositions. In studying the process of glass solidification, a series of experiments was conducted for glasses of the same composition but variable diathermancy, determined on the basis of absorption in the region of the wavelength 1100 nm using a spectrophotometer. Compounds containing Co, Cr, Fe, and Ni were used to vary the light absorption level.

Molding under isothermal conditions. Shaping of products at a constant temperature proceeds under the effect of surface forces and gravity, and after that the glass melt is cooled and solidified. In one case, the surface forces act as the molding force (production of small spheroid articles like microscopic balls, beads, etc.) and in another case, the molding factor is gravity, with the surface forces acting as a limiting factor (spread of fluid glass on metal melt) [10]. In both cases, the process rate depends on the glass melt viscosity.

In molding small spheroid articles, the tension force P_σ imparts a required shape to the glass melt and preserves this shape, counteracting the gravity force P_g . The viscous-resistance force P_η in this case determines the process rate. In the case of uniform heating, the surface force P_σ affects the entire bulk of the product. In the case of partial melting of the glass (thermal polishing of the surface), the movement of the glass melt under the effect of the surface tension force can be considered as spreading on a solid substrate with virtually perfect wetting of the substrate by the melt [11, 12]. In this case $P_\sigma \gg P_g$.

The relationship between the surface forces determined by Laplace pressure and the pressure determined by gravity for a sphere can be expressed as follows:

$$\frac{P_\sigma}{P_g} = \frac{2\sigma/r}{mg/(\pi r^2)} = \frac{3\sigma}{2r^2\rho g},$$

where σ is the surface tension of the glass melt; r is the sphere radius; m is the mass of the glass melt (article); g is the free-fall acceleration; ρ is the glass melt density.

With the sphere radius 10^{-3} m, the surface tension 0.33 N/m, and the density 2300 kg/m³, the surface force is 22 times greater than the force of gravity, whereas with the radius 5×10^{-4} m, it is 88 times greater.

The relationship for other spheroid articles is determined in a similar way, taking into account their shape.

In float glass technology, the glass melt spreads over the metal melt under the effect of gravity, and $P_g \gg P_\sigma$. However, the surface forces limit the spreading until a lens of a certain equilibrium thickness is formed:

$$h = \sqrt{\frac{2L\rho_1}{g\rho_2(\rho_1 - \rho_2)}}. \quad (1)$$

where h is the glass lens thickness; L is the spreading coefficient, $L = \sigma_2 + \sigma_{12} - \sigma_1$; ρ_1 and σ_1 are the density and the

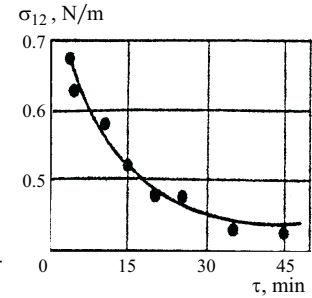


Fig. 3. Kinetics of interfacial-tension variation.

surface tension of the metal; ρ_2 and σ_2 are the density and the surface tension of the glass melt; σ_{12} is the interfacial tension.

The relationship between the principal acting forces is important for determination of the rate of isothermal molding. The generalized formulas have the following form:

$$P_\sigma = A \frac{\sigma}{r}; \quad P_\sigma = B \frac{m}{S}; \quad P_\eta = C \frac{\eta}{\tau}.$$

where A , B and C are coefficients; S is the article cross-sectional area; η is the glass melt viscosity; τ is the time of article formation (shaping).

A comparison of these formulas reveals the static nature of surface tension and gravity and the kinetic nature of viscous resistance. Assuming that the surface and gravity forces are expended on overcoming the viscous resistance of the glass melt, the process duration can be found from the formula

$$\tau_\sigma = Kr \frac{\eta}{\sigma}; \quad \tau_g = MS \frac{\eta}{m}, \quad (2)$$

where K and M are coefficients.

Formulas (2) characterize the technological relationship of the isothermal molding factors. They can be used to design the processes of molding small spheroid articles, fusion of edges, and thermal polishing of a surface, as well as glass melt spreading on various substrates.

High viscosity of the glass-melt and kinetic character of viscous resistance result in nonequilibrium values of surface and interface tension.

Figure 3 shows the variation of the interfacial tension in the glass-tin system at a temperature of 1200°C.

Interfacial-tension values that exceed the equilibrium values are registered when the contact duration is shorter than the time needed to establish the adsorption equilibrium on the interphase boundary. Such interfacial-tension values are also found in practical experience in the float process. Paper [10] describes a glass band of equilibrium thickness. However, the analysis of formula (1) shows that the equilibrium thickness of a glass band or a glass lens is determined by the circumstance that the interfacial-tension values exceed the equilibrium values. This is related to the high viscosity of the glass melt and the limited duration of its existence in the zone in which a layer of equilibrium thickness is formed. Therefore, regarding the float process, it is more ap-

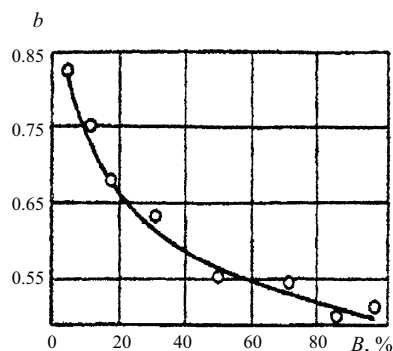


Fig. 4. Dependence of the coefficient b in equation (3) on the absorption B at the wavelength 1100 nm.

appropriate to characterize the glass lens thickness or the glass band thickness as equilibrium in the technological sense.

Molding under nonisothermal conditions. In this case, the shape of the articles is formed due to the effect of external forces (drawing, rolling, compression, blowing) using limiting bodies (debiteuse, rolls, molds, etc.). In doing so, the glass melt undergoes complex heat exchange with the ambient medium and is continuously solidified.

Solidification starts from the glass melt surface and then expands to the entire bulk. In this context, the curing process can be represented as having two stages: emergence of localized sites with increased glass viscosity; formation of an arbitrary interphase boundary and migration of this boundary into the glass depth. The relationship between the surface and volumetric factors in glass melt solidification is discussed in [13].

An experimental check as well as the use of data from [14] demonstrated the validity of the obtained relationship.

The volumetric solidification kinetics can be revealed via the thickness of a glass layer of a preset viscosity. Thus, in evaluating the final solidification of glass of viscosity 10^{12} Pa · sec, the volumetric rate of solidification can be characterized by the rate of migration of an elementary glass melt layer of viscosity 10^{12} Pa · sec into the glass depth. In practice, this stage of the process can be assessed by the distance from the glass surface to which the elementary glass layer of viscosity 10^{12} Pa · sec shifts in a certain time period. Studies of the processes of glass cooling and curing under different conditions indicated that the kinetics of volume solidification of glass in general form is expressed as follows:

$$\delta = a\tau^b, \quad (3)$$

where δ is the arbitrary thickness of the solidifying layer; a and b are coefficients.

It should be noted that the coefficient b indicates the type of heat transfer in glass curing. For true thermal conductivity $b = 0.5$; when the heat transfer includes heat transfer by radiation, the value of b increases.

As was mentioned earlier, a series of experiments was conducted for glasses of the same composition varying in

their diathermancy, which was determined based on the light absorption in the region of the wavelength 1100 nm. The results of the experiments are shown in Fig. 4. The value of the coefficient b keep decreasing with increasing light absorption at the wavelength 1100 nm. In glasses with low diathermancy, this parameter approaches $b = 0.5$, which is an indication of the prevalence of heat conduction in the heat transfer.

The use of data from [14, 15] to determine the coefficient b corroborates the well-known statement that the role of heat conduction increases under a high rate of cooling and a small thickness of the glass layer.

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